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INVESTIGATION OF THE PHOTOLUMINESCENCE SPECTRA OF RARE-EARTH ELEMENTS IN PORES OF AN OPAL MATRIX

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The main idea of this paper is researching the light emission of Eu^{3+} and Dy^{3+} in an opal matrix. The opal synthesis was carried out using Stöber method. The size of globules calculated from the transmission spectrum of prepared samples is equal to 231 nm. The samples were infiltrated with rare-earth element oxides in concentrated solution of nitric HNO_3 and perchloric HCl acids in the ratio 3:1. Next, the samples were heated to 100°C to reduce the relative content of water. The spectra of photoluminescence in the range 420-640 nm were excited by a semiconductor laser with λ=405 nm at the radiation registration along the direction of growth [111]. In the spectrum of the sample infiltrated by europium, there are distinctive europium lines at 580, 593 and 618 nm, which correspond to the typical transitions of this rare-earth element, such as $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$ i $^5D_0 \rightarrow {}^7F_2$. Distinctive spectral lines of dysprosium luminescence are at wavelengths of 480 and 572 nm. The maxima of these wavelengths correspond to the typical lines of luminescence of trivalent dysprosium – specifically, transitions $^4D_{9/2} \rightarrow {}^6H_{13/2}$ i $^4D_{9/2} \rightarrow {}^6H_{11/2}$. The influence of photonic crystalline effects on the photoluminescence spectra of the obtained samples is studied.

Keywords: photonic crystal, synthetic opal, infiltration, rare-earth element, luminescence spectrum, energy transitions.

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1. Introduction

In recent years, we have witnessed rapid growth in quantity of consumers and consequently in the number of optic communication systems' manufacturers. Optical fibre technology can provide the transmission of large amounts of telecommunication and Internet data packets over long distances with a low loss rate. Provision of high-quality information transfer requires good active laser medium. Photonic crystals, which are artificial crystals composed of periodic dielectric structures and forbidden electronic energy bands, can be used for this purpose. The bands contained therein prevent the propagation of light waves of a specific frequency range. Synthetic opal is an example of photonic crystal structure. Structurally it is a globular photonic crystal. The spaces between globules, called pores, are connected by channels and create a regular sublattice [1]. The creation and investigation of the optical properties of new luminescence materials based on synthetic opals and rare-earth elements is of both fundamental and practical interest. Photonic crystals infiltrated by rare-earth elements are perspective active media, which can become a basis for the construction of a new devices in such industries as laser technology, optoelectronics, and nonlinear optics. The combination of the photonic crystal properties of synthetic opals and narrow bands in the luminescence spectra of rare-earth elements makes it possible to create new light sources with unique properties: amplification and spatial redistribution of the emission intensity [2, 6].
The main idea of this work is studying the photoluminescence spectra of samples of synthetic opals infiltrated with oxides of rare-earth elements (Eu_2O_3, Dy_2O_3).

2. Experiment

Synthesis of opals was carried out according to the Stöber method. For this purpose we used silicon dioxide-based microparticles. Spherical particles were made through the hydrolysis reaction of tetraethyl orthosilicate ether $Si(OC_2H_5)_4$ (TEOS) in ethyl alcohol. Ammonia was used as the catalyst [1].

After merging the ethyl alcohol with ammonia and water, TEOS is added to the mixture. Slightly stirred, the solution is left to evaporate the liquid. This process can take up to 8 months. The synthetic opals made by the method of natural sedimentation contain about 15 %

of water and residual organic matter. To minimize the destruction and content of water and organic materials, samples were heated to a temperature of 800°C. Pores of the finite synthetic opal samples were infiltrated by rare-earth elements – namely, europium and dysprosium. This process was carried out using the infiltration of the concentrated solutions of rare-earth element oxides (Eu_2O_3 and Dy_2O_3) in aqua regia (solution of nitric HNO_3 and perchloric HCl acids) into the samples. Next, the samples were heated to 110°C for an hour. The goal of this step was the evaporation of the liquid accumulated in synthetic opals through the process of infiltration. Examination of transmission and luminescence spectra was performed with the spectrometer based on DFS-12. The spectra of photoluminescence in the range 420-640 nm were excited by a semiconductor laser with λ_{ex}=405 nm. Fig. 1 shows the geometry of photoluminescence (in the case on Fig. 2 and Fig. 3 the observation was along [111] direction).

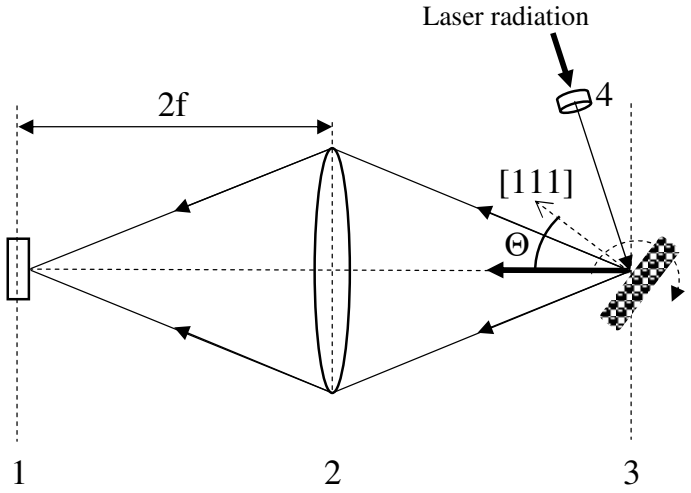

Fig. 1. The geometry of photoluminescence measurement (top view):
1 – spectrometer based on DFS-12, 2 – lens, 3 – sample, 4 – beam collimator.

Fig. 2 shows the transmission spectrum of the synthetic opal sample. The sample reaches a transmission minimum at a wavelength of 510 ±50 nm. The distance between the layers of synthesized opals in this case is 189 nm, and the globule size is 231 nm.

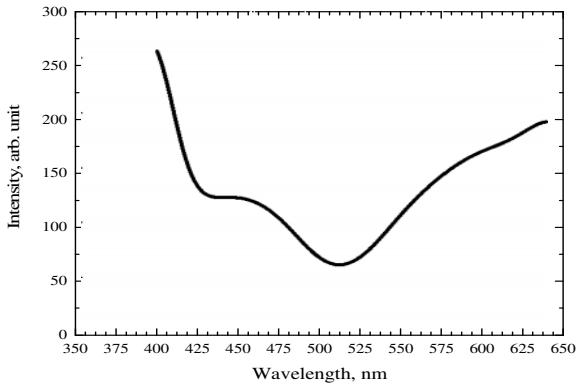

Fig. 2. The transmission spectrum of the synthetic opal sample (in [111] direction).

The investigation of photoluminescence spectra was carried out on samples of synthetic opals, which have the diameter of globules of 231 nm. The samples were infiltrated with rare-earth element oxides in the concentrated solution of nitric HNO_3 and perchloric HCl acids in the ratio 3:1. Also the opal sample with dysprosium was additionally infiltrated with europium oxide.

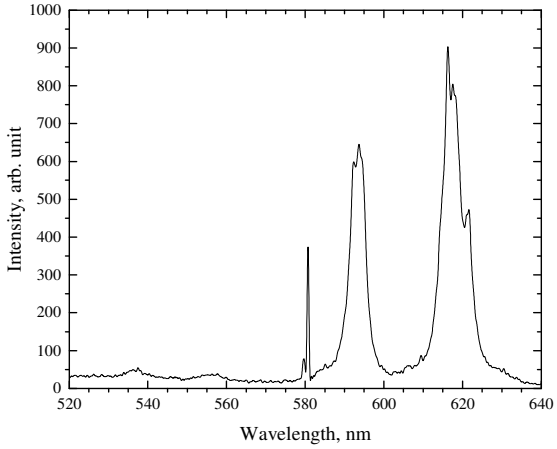

Fig. 3. The photoluminescence spectrum of opal sample infiltrated with europium oxide.

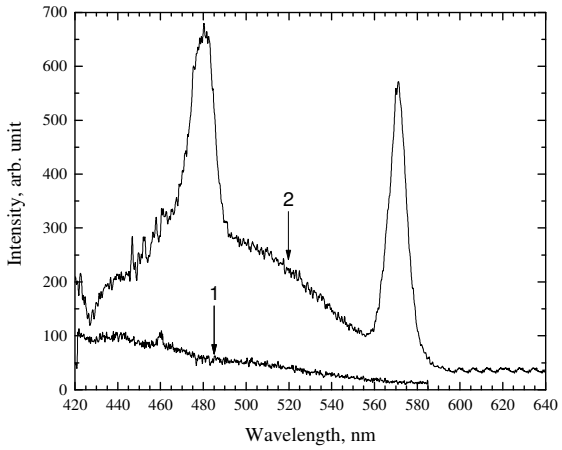

Fig. 4. The photoluminescence spectrum of opal sample infiltrated with dysprosium oxide: 1 – initial opal sample; 2 – opal sample infiltrated by dysprosium oxide.

3. Results and discussions

In the spectrum of the sample infiltrated by europium (Fig. 3) there are distinctive europium lines at 580, 593, and 618 nm, which correspond to the typical transitions of this rare-earth element, such as $^5D_0 \rightarrow {}^7F_J$ where J = 0, 1, 2 [3, 4, 7]. Distinctive spectral lines of dysprosium luminescence at wavelengths of 480 and 572 nm are shown in the Fig. 4. The maxima of these wavelengths correspond to the typical lines of luminescence of trivalent dysprosium – specifically, transitions $^4D_{9/2} \rightarrow {}^6H_J$ where J = $\frac{13}{2}$ and $\frac{11}{2}$ [2, 8, 9].

The luminescence spectrum in Fig. 4 has a wide band in the range of 420-560 nm, which is not present in initial and infiltrated by europium opal samples. It can be caused by the glow of the defects in opal matrix appeared as a result of dysprosium oxide infiltration [5].

Fig. 5 shows a detailed study of the luminescence spectrum of the sample infiltrated with europium.

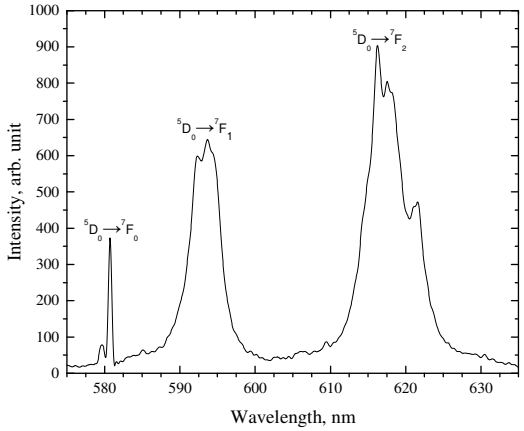

Fig. 5. The photoluminescence spectrum of the sample infiltrated with europium with distinctive europium lines at 580, 593, and 618 nm, which correspond to the typical transitions of this rare-earth element, such as $^5D_0 \rightarrow ^7F_J$, where J = 0, 1, 2.

After the analysis of luminescence of synthetic opal samples infiltrated with rare-earth elements, one additional rare-earth element was infiltrated into these samples.

Fig. 6 shows the dependence of the luminescence spectrum of opal sample with dysprosium on the angle of exciting radiation incidence.

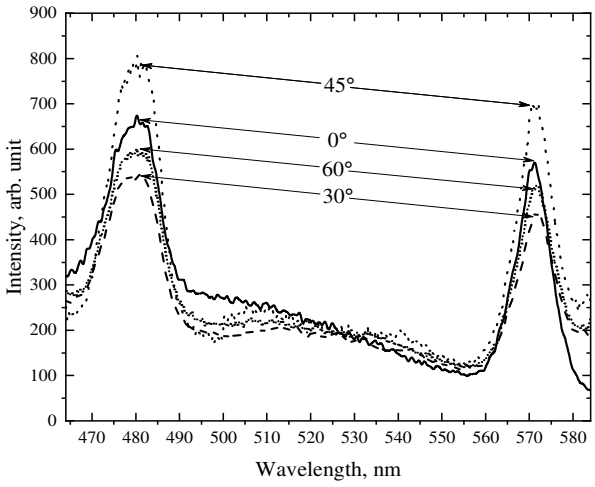

Fig. 6. Angular dependence of the photoluminescence spectra of the opal sample infiltrated with dysprosium oxide. The measurements were carried out depending on the angle between the direction of observation and the [111] direction.

Obtained spectra show distinctive dysprosium transitions $^4D_{9/2} \rightarrow {}^6H_{13/2}$ and $^4D_{9/2} \rightarrow {}^6H_{11/2}$ at wavelengths of 480 and 572 nm [8].

In Fig. 5 (angle 45°) we can see a sharp increase in the intensity of the spectral lines of the dysprosium luminescence.

A sharp increase in the intensity of spectral lines of luminescence can be explained by the collision of radiation with the edges of forbidden band of the opal composite with dysprosium [1, 3, 4].

Further, the sample of opal with dysprosium was additionally infiltrated with europium. Fig. 7 shows the luminescence spectrum of the opal-dysprosium-europium sample.

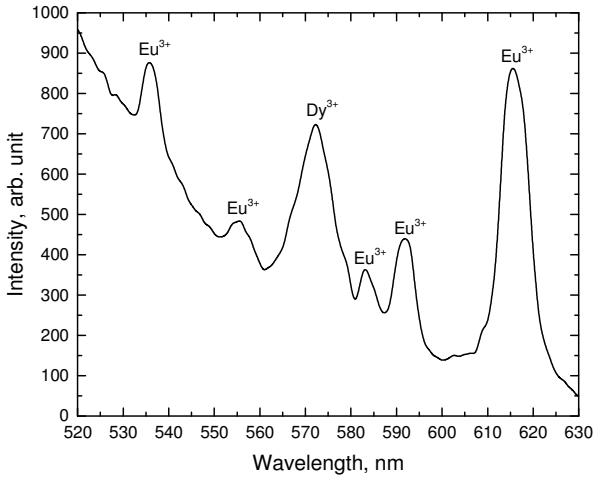

Fig. 7. – The photoluminescence spectrum of opal-dysprosium-europium sample.

The figure shows typical spectral lines of dysprosium – 572 nm, and europium – 535, 555, 583, 592, and 615 nm. The lines of both rare-earth elements are presented in this spectrum [2, 4, 8].

The luminescence spectra of the samples infiltrated with dysprosium and europium show clearly the lines of luminescence upon laser excitation at a wavelength of 405 nm [10].

4. Conclusions

1. The most intensive photoluminescence is observed for ions Eu^{3+} in opal pores.

2. The spectral line at 480 nm in the photoluminescence spectrum of the opal sample, which is infiltrated with Dy^{3+}, is located on the broadband radiation background. It can be caused by the glow of the defects in opal matrix appeared as a result of dysprosium oxides infiltration.

3. The angular dependences of the photoluminescence spectra of opal-Dy^{3+} samples is measured. The radiation intensity at the angle 45° increases for spectral transitions $^4D_{9/2} \rightarrow {}^6H_{13/2}$ and $^4D_{9/2} \rightarrow {}^6H_{11/2}$ at 480 nm and 572 nm wavelengths, respectively. An increase in the intensity of the spectral lines of photoluminescence can be explained by the increase in the density of optical states due to the emission of radiation to the

boundary of the synthetic opal stop-band, which undergoes a short-wave shift by 18 nm when the angle of observation is changed by 45º.

4. In spectra of samples infiltrated with two rare-earth elements, namely dysprosium and europium, there are photoluminescence lines of both dysprosium and europium.

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